

PURIFICATION OF LACTIC ACID

Production of Methyl Lactate from Aqueous Solutions of Crude Acid

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Difficulties involved in the purification of fermentation lactic acid are outlined, and a new method for purifying this acid or preparing methyl lactate directly from crude aqueous lactic acid is described. The method comprises passing methanol vapor through aqueous lactic acid and condensing the effluent vapors. The condensate, a mixture of methanol, water, and methyl lactate, can be distilled to recover the methyl lactate or hydrolyzed to obtain purified lactic acid. Other esters of lactic acid can be prepared similarly with appropriate alcohols. The effect of variables on the volatilization of lactic acid (principally as the methyl ester) with methanol vapor has been studied. The time required to volatilize a given amount of lactic acid decreases as the rate of methanol addition is increased. Increasing the catalyst concentration (concentrated sulfuric acid) accelerates the operation. Approximately 9 moles of methanol are required to volatilize 1 mole of lactic acid from an 82% solution of the acid (kept at 92–100° C.) over a wide range of methanol addition rates. Although dilute lactic acid can be used, less time and less methanol are required to volatilize a given quantity of lactic acid from the more concentrated solutions.

A CONSPICUOUS feature of the lactic acid industry (18, 24) is that this acid is sold as several different grades and at prices considerably higher than the cost of the sugars used as raw materials in its fermentative production (19). Although the sugars in whey, molasses, and starch hydrolyzates sell for about 1 to 4 cents per pound (27) and yield almost one pound of lactic acid (25) for each pound of sugar, the crude and U.S.P. grades of lactic acid are quoted at 11 and 43 cents per pound (100% basis), respectively (15).

Since lactic acid, as it occurs in dilute fermentation liquors, is inexpensive, the high cost of relatively pure lactic acid may be attributed largely to difficulties encountered in purification.

The purification of fermentation lactic acid is difficult because of its low vapor pressure, tendency to undergo self-esterification (5), similarity in solubility characteristics to water, and presence of troublesome impurities (1, 9, 17, 19, 24), such as dextrans, proteins, inorganic salts, and unfermented sugars.

Six types of purification procedures were reviewed recently by Smith and Claborn (24), who recommended conversion (32) of calcium lactate into methyl lactate, purification of the methyl ester by distillation, and hydrolysis of the ester (33). Other proposed purification methods comprise crystallization of the calcium (3, 13, 16, 31), aniline (2), or zinc salt (24, 30), extraction (8, 28, 29) with a solvent such as isopropyl ether (7), and distillation (24). Some of the impurities in lactic acid produced by fermentation can be removed or destroyed by treatment with oxidizing agents (24) such as hypochlorites, chromates, permanganates, nitric acid, peroxides, chlorine, and ozone.

Distillation procedures have been studied by previous investigators to determine their merit in the purification of lactic acid. Distillation in a vacuum (10, 26), steam distillation under reduced pressures (6, 11, 12, 21, 22), distillation in a stream of gas (14), and passage of superheated steam through condensation polymers of lactic acid (17) have been described as purification procedures. Since lactic acid of good quality is still relatively expensive (15), it appears that the distillation and other purification methods are not entirely satisfactory in their present stage of development and that improved purification procedures are needed.

Previous communications (5, 20) from this laboratory have shown that methanol reacts readily with condensation polymers of lactic acid, methyl lactate is readily volatilized in a stream of methanol vapor, and methyl lactate and water distill azeotropically. These facts seemed to warrant an investigation of the preparation and removal of methyl lactate from aqueous solutions of lactic acid by passing methanol vapor through the solution. The present paper indicates that this technique is advantageous in several respects for preparing methyl lactate (or

TABLE I. VOLATILIZATION OF LACTIC ACID WITH ALCOHOL VAPORS

Expt. No.	Lactic Acid		Alcohol	H ₂ SO ₄ , Ml.	Tower Temp., °C.	Time, Hours	Available Lactic Acid ^a , %	
	Moles	Concd., %					Volatilized	Retained in tower ^b
1	1.0	82°	Methyl	1	93-112	1.6	99.5	..
2	1.0	82°	Methyl	0.5	97-102	2.0	91	..
3	1.0	82°	Methyl	0.25	99-106	2.5	103	..
4	1.0	82°	Ethyl	0.5	102-113	3.75	97	..
5	1.0	82°	Isopropyl	0.5	97-108	7.0	86	..
6	1.0	82°	Methyl	0.5	97-108 ^d	4.0	78	..
7	0.5	35°	Methyl	0.5	84-109	4.66	88	6
8	1.13	57°	Methyl	1	96-100	4.75	74	..
9	1.0	57°	Methyl	1	98-107	3.2	87	9
10	0.93	26°	Methyl	1	98-107	4.23	86	..
11	0.93	26°	Methyl	1	98-105	3.91	93	..
12	1.0	26°	Methyl	1	106-112	4.0	81	..
13	1.0	26°	Methyl	1	ea. 100	4.0	95	..
14	1.0	26°	Methyl	1	64-128	5.0	100	..
15	1.0	26°	Methyl	1	98-106	4.42	95	..
16	2.0	26°	Methyl	2	95-105	8.1	95	..
17	2.0	56°	Methyl	2	118-127	2.83	91	..
18	2.0	103°	Methyl	2	94-100	5.66	97	..
19	1.0	26°	Ethyl	1	98-127	3.67	82	..
20	1.0	26°	Ethyl	1	98-125	7.25	85	..
21	1.0	26°	Isopropyl	1	117-126	11.33	52	..
22	1.0	48°	Ethyl	1	96-118	4.75	82	13
23	1.0	81°	Methyl	1	94-104	3.0	96	..
24	1.0	89°	Methyl	None	94-101	9.33	64	30
25	1.0	89°	Methyl	None	121-127	5.0	76	16
26	1.0	89°	Methyl	None	144-154	4.0	82	13
27	1.0	89°	Isoamyl	1	101-106 ^m	5.25	45	46
28	1.0	89°	Methyl	"	95-107	4.0	69	26
29	1.0	91°	Methyl	0.5	97-105	4.0	70	..
30	1.0	91°	Methyl	1	97-104	2.33	74	21
31	1.0	91°	Methyl	1	101-109	6.0	77	20
32	1.0	91°	Methyl	2	101-108	2.75	82	17
33	1.0	91°	Methyl	2	101-108	2.67	85	15
34	1.0	91°	Methyl	3	99-109	3.16	90	13
35	1.0	91°	Methyl	3	91-108	3.0	92	9
36	1.0	91°	Methyl	4	92-106	2.66	94	9
37	2.0	89°	Methyl	4	88-105	3.2	97.5	..
38	1.0	91°	Ethyl	1	99-107	3.25	73	25
39	1.0	91°	Ethyl	1	96-107	4.75	78	19
40	1.0	91°	Ethyl	1	96-107	6.0	78	16
41	1.0	91°	Isopropyl	1	97-109	9.9	59	40

^a No correction made for possible presence of acidic compounds other than lactic acid and its esters.

^b Tower washed with water or methanol at end of experiment, and washings titrated.

^c Almost colorless edible lactic acid obtained from the Du Pont Company.

^d Reaction tower operated under pressures of 110 to 114 mm. of mercury.

^e Fermentation liquor, furnished by Du Pont, was acidified with sulfuric acid and filtered; filtrate was concentrated to 35% lactic acid.

^f Crude lactic acid supplied by Sealtest, Inc.

^g Crude lactic acid supplied by Sheffield Farms Company, Inc.

^h Prepared by concentration of 26% crude lactic acid used in experiments 10 to 16.

ⁱ Prepared by concentration and filtration of 26% crude lactic acid used in experiments 10 to 16.

^j Crude lactic acid supplied by American Maize-Products Company.

^k Technical lactic acid supplied by Clinton Company.

^l Prepared by concentration and filtration of 22% crude lactic acid obtained from Clinton Company.

^m Reaction tower operated under a pressure of 60 to 65 mm.

ⁿ 2.5 grams of H₂BO₃ as catalyst.

^o 3.5 grams of *p*-toluenesulfonic acid as catalyst.

heated to hydrolyze the lactic ester and distill the alcohol. In some experiments the condensate was distilled, usually in a vacuum, to recover the lactic ester.

In one series of experiments (Table I), lactic acid and alcohol vapor (usually methanol) were passed countercurrently through a tower. This comprised a Pyrex tube, 1 inch in diameter and 4 feet long, packed with 1/4-inch Berl porcelain saddles. The top of the tower had an inlet tube for introducing the crude lactic acid and an outlet tube for removing vapors. The base of the tower was provided with a side arm for introducing the alcohol vapor. The tower was heated electrically, and the temperature was controlled and recorded automatically. The crude lactic acid, with or without an esterification catalyst, was fed in at the top of the tower, and alcohol vapor was introduced at the base. The vapors from the tower, composed essentially of alcohol, water, and lactic ester, were led to a continuous stripping still, and the major portion of alcohol was separated and automatically returned through a liquid seal to the alcohol vaporizer. The purified lactic acid-lactic ester solution was collected at the base of the stripping still. Titration and saponification data were obtained to estimate the amount of lactic acid that had been carried over, principally as an ester, by the alcohol vapor. The condensate, when slowly distilled to hydrolyze the lactic ester and remove the alcohol, yielded a purified aqueous solution of lactic acid. During hydrolysis, the virtually colorless lactic acid sometimes became pale yellow or amber. It was found, however, that the color can be almost completely removed by treatment with a fraction of 1% of decolorizing carbon.

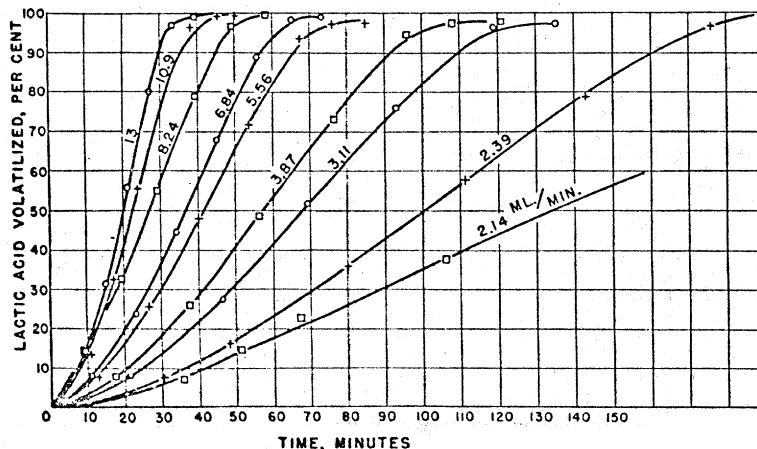
Operation of the tower may be illustrated by experiment 9 (Table I). To 159 grams (1 mole) of crude 57% lactic acid was added 1 ml. of concentrated sulfuric acid. The resulting mixture was fed into the top of the tower, and methanol vapor was introduced at the base. The condensate, collected at the base of the stripping still, was refluxed during the run to accelerate hydrolysis. The temperature of the tower was 98° to 107° C. After 3 hours and 10 minutes, over 87% of the lactic acid in the crude had reacted with methanol, and the product had distilled and collected at the base of the stripping column. The hydrolysis of the lactic ester in the purified solution was completed by slow distillation until the vapor temperature reached 97° C. under total reflux. A virtually colorless aqueous lactic acid solution of approximately 57% concentration was obtained.

The effect of certain variables was determined with an almost colorless edible 82% lactic acid, using a cylindrical Pyrex vessel with a fritted glass plate at the bottom. One mole of the 82% lactic acid (containing sulfuric acid) was placed in the cylindrical vessel (8.5 inches high and 2.75 inches in diameter), which was surrounded by a boiling water bath. Methanol, contained in a

certain other lactic esters) from crude, dilute lactic acid and for purifying lactic acid through its methyl ester. Wenker (33) and Schopmeyer and Arnold (23) also purified lactic acid by passing alcohol vapor through the crude acid; their patents appeared after the completion of this investigation.

PURIFICATION PROCEDURE

Alcohol vapor was passed through the crude lactic acid, which was maintained at a temperature above the boiling point of the alcohol. The lactic ester thus formed was volatilized in the stream of alcohol vapor, and the mixture of alcohol, water, and alkyl lactate was condensed. The fact that some of the lactic esters distill azeotropically (20, 32) with water may facilitate volatilization of the ester. When purified lactic acid was desired, the condensate was



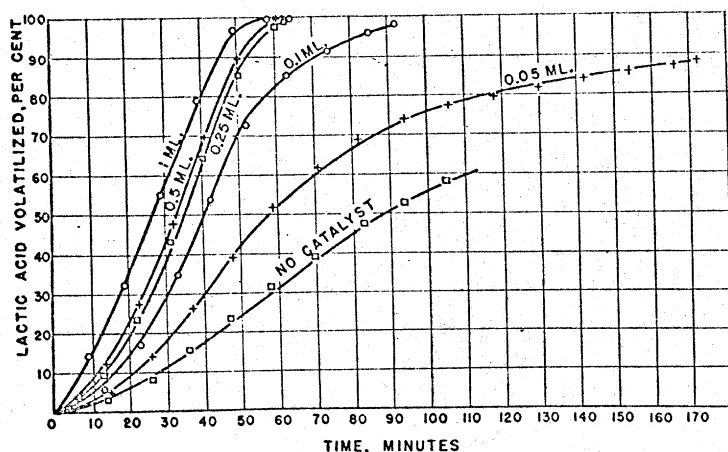


Figure 2. Effect of Catalyst Concentration (Milliliters of Concentrated Sulfuric Acid per Mole of 82% Lactic Acid) on Rate of Volatilization of Lactic Acid

graduated cylinder, was pumped with a constant-rate bellows pump (4) through a steam-jacketed preheater into the bottom of the lactic acid solution. The vapors withdrawn from the top of the cylindrical reaction chamber were condensed in approximately 100-ml. portions. These portions were titrated to determine the lactic acid volatilized principally as methyl lactate. In some instances the condensates were distilled to recover the methyl lactate. A suitable distillation procedure consisted in distilling most of the methanol, adding an entraining agent such as benzene, distilling water azeotropically, and then distilling the methyl lactate under reduced pressure.

The temperature of the lactic acid solution rose sharply to approximately 108° or 109° C. in the first minute or two of these experiments, although heat was supplied by a boiling water bath. This elevation of temperature may have been due to esterification of the carboxyl groups or to heat of solution. After the initial increase, the temperature of the mixture dropped to approximately 92–95° (depending on the feed rate) and then gradually rose to 100° C. at the end of the experiment.

Methyl lactate was isolated from the condensates in 85 to 90% yields by adding a small quantity of sodium acetate, distilling the methanol at atmospheric pressure, adding benzene, distilling water and benzene, and finally recovering the methyl lactate by vacuum distillation. When calculated on the basis of the lactic acid not recovered as polylactic acid in the distillation residues, the yields of methyl lactate were over 90%.

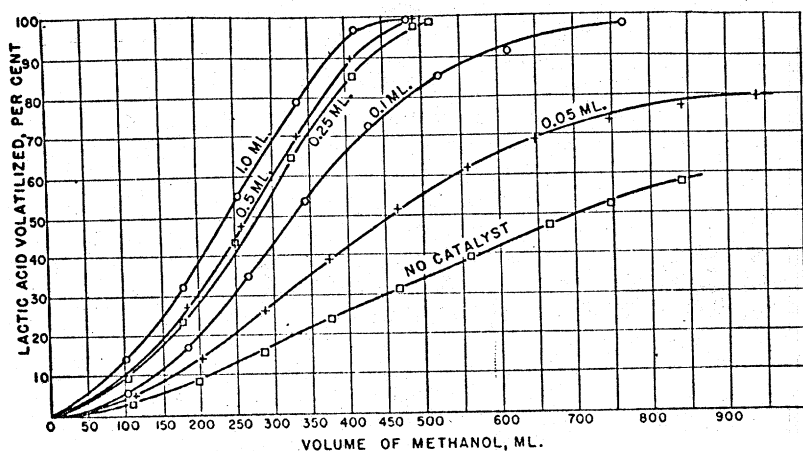


Figure 3. Effect of Catalyst Concentration (Milliliters of Concentrated Sulfuric Acid per Mole of 82% Lactic Acid) on Volume of Methanol Required for Volatilization (Methanol Feed Rate, 8 to 8.3 ML. per Minute)

PACKED TOWER EXPERIMENTS

Results obtained by passing crude lactic acid and alcohol vapors countercurrently into a packed tower show that lactic acid can be readily volatilized as ester in high yields by this procedure (Table I). The method is applicable to different types of crude lactic acid and to various concentrations. This and the fact that either methyl lactate or purified lactic acid can be produced illustrate the flexibility and usefulness of the method.

The crude lactic acid used may be the dilute aqueous solution obtained by liberation of lactic acid from the fermentation liquor, or the product obtained by concentration of such a solution to any convenient content of lactic acid. One advantage in first concentrating the dilute aqueous solution lies in the fact that the more concentrated solution appears to react more rapidly with alcohol vapors than does the dilute solution. Furthermore, the inorganic salts and other solid impurities precipitated by concentration can be removed by filtration, although this is not necessary. Crude lactic acid solutions ranging in acid content from 26 to 103% (by weight) of lactic acid have been used with 90 to 100% of the acidity esterified by methanol vapor to form a volatile product. The lactic acids of higher concentration, which contained some condensation polymers of lactic acid, were prepared by removing water from the more dilute solutions.

In the purification of lactic acid, the alcohol vapors may be reacted with the crude acid either in the presence or absence of esterification catalysts. In the absence of esterification catalysts, the reaction is much slower. By using relatively large amounts of esterification catalyst, the yield of acid volatilized was considerably improved. The yield was raised to 97% by use of 4 ml. of concentrated sulfuric acid per mole of crude lactic acid (experiments 24, 25, 29–37). Boric acid and *p*-toluenesulfonic acid were effective as catalysts, but they had no obvious advantage over sulfuric acid. It was noted that some of the catalyst, either as such or as a derivative, was carried over by the alcohol vapor when boric acid or sulfuric acid was used. Hence, in making edible grades of lactic acid, it may be advisable to purify the lactic acid in the absence of a catalyst, use a harmless catalyst, neutralize the mineral acid in the purified product, or revolatilize the lactic acid in a second tower.

In experiments 24 to 26 the use of higher temperatures increased the yield of volatilized acid in the absence of a catalyst. Less time was required for the volatilization at the higher temperatures.

Different types of alcohol may be employed. Methanol or ethanol vapors seemed equally satisfactory. Isopropyl alcohol was not so suitable as methanol or ethanol (experiments 5, 21, and 41). When methylallyl and isoamyl alcohols were used, the experiments were conducted at reduced pressure, mainly to avoid the use of high temperatures.

FERMENTATION LIQUOR

That the process can be used even with crude unfiltered fermentation liquors was shown by the experiments of Table II, conducted as follows: The crude liquor, acidified with sulfuric acid, was placed (with or without filtering) in a flask having an entrance tube extending to the bottom of the flask and an exit tube attached to a condenser. The flask was immersed in a boiling water bath. Methanol vapor, produced by vaporizing methanol in another flask, was led in through the entrance tube. The exit vapors, composed essentially of methanol, water, and methyl lactate, were condensed. Saponification of the condensate,

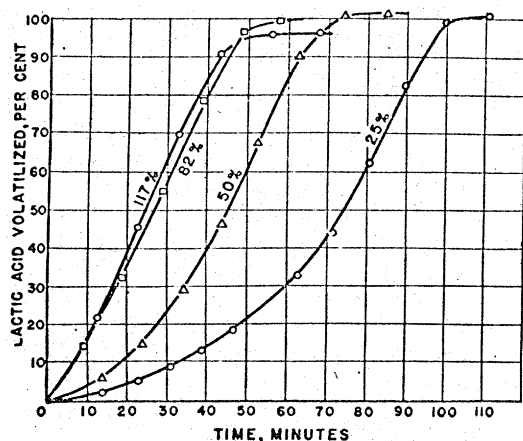


Figure 4. Effect of Lactic Acid Concentration on Rate of Volatilization (Methanol Feed Rate 8 to 8.3 Ml. per Minute)

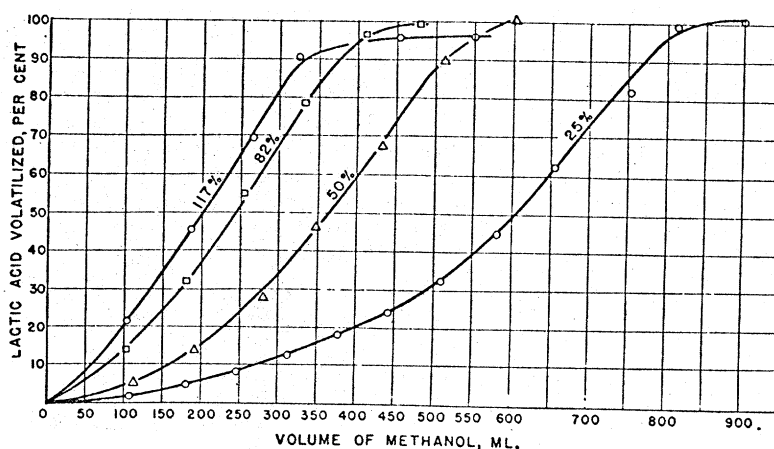


Figure 5. Effect of Lactic Acid Concentration on Volume of Methanol Required for Volatilization

which was colorless, showed that most of the lactic acid, mainly as its ester, had been volatilized by the methanol vapor. To the condensate was then added 0.25 to 0.5 gram of sodium acetate, and methanol was distilled at atmospheric pressure (vapor temperature, 85–90° C.). Then 100 ml. of benzene were added, and water was removed by continuous entrainment using a modified Dean and Stark trap. After all the water had been removed, the benzene was distilled at atmospheric pressure, and then methyl lactate was recovered by distillation under approximately 30 mm. pressure.

TABLE II. METHYL LACTATE AND PURIFIED LACTIC ACID FROM FERMENTATION LIQUORS^a

Expt. No.	Fermentation Liquor			H ₂ SO ₄ , Ml. ^b	Re-action Time, Hours	Temp., ° C.	% Lactic Acid Volatilized ^c	Methyl Lactate % ^d
	% Ca lactate	Amount	Lactic acid equivalent					
1 A	ca. 10	510 cc.	0.5	0.5	3.0	98	75	..
2 A ^e	ca. 10	510 cc.	0.5	0.5	4.6	84–109	88	..
3 B ^e	10.2	1070 g.	1.0	2.0	4.5	80–95	87	78
4 C	10.5	1037 g.	1.0	1.0	7.6	90–96	82	56
5 C	10.5	1037 g.	1.0	10.0	7.0	88–95	93.5	81
6 C ^e	10.5	1037 g.	1.0	1.0	2.5	90–97	96	91
7 C ^e	10.5	1037 g.	1.0	1.0	2.5	90–97	93	85

^a Kindly supplied by Du Pont Company.

^b In excess of that required to liberate lactic acid from calcium lactate.

^c Determined by titration and saponification of condensate.

^d Isolated by distillation; based on lactic acid originally present in fermentation liquor.

^e The acidified liquor was filtered, and the filtrate concentrated (to approx. 35% in expt. 2 and 3, and over 90% in expt. 6 and 7) prior to treatment with methanol.

In experiments 4 and 5, where dilute fermentation liquor was used, lactic acid instead of methyl lactate was obtained owing to hydrolysis of the ester during the removal of water. However, a second treatment of this lactic acid with methanol vapor gave the yields of methyl lactate indicated—i.e., 56 and 81%, respectively.

The data of Table II show that volatilization of lactic acid and formation of isolable methyl lactate are facilitated by the use of considerable excess of sulfuric acid; a high yield of methyl lactate resulted when 10 ml. of sulfuric acid in excess of that required to neutralize the calcium lactate were used. A high yield was obtained also by filtering the acidified fermentation liquor and concentrating the filtrate prior to treatment with methanol vapor. The latter procedure has the advantage that most of the water is distilled only once.

EFFECT OF VARIABLES

Data on the effect of quantity of methanol used, methanol feedrate, concentration of lactic acid, and concentration of catalyst were obtained by pumping methanol through lactic acid contained in a gas-washing cylinder. Figure 1 shows that the rate of volatilization of lactic acid from an 82% lactic acid solution containing 1 ml. of concentrated sulfuric acid increases with increase in the rate of methanol addition. Probably the limiting factors are the rates of esterification and alcoholysis (of polylactic acid), which apparently occur rapidly when lactic acid and methanol are the reactants.

Figure 2 indicates that, when the concentration of the catalyst is below 0.2 ml. of concentrated sulfuric acid per mole of lactic acid, the rate of volatilization is materially retarded. In these experiments the methanol was passed into the lactic acid mixtures at the fairly rapid and constant rate of 8.0 to 8.3 ml. of liquid per minute. Probably volatilization at the lower catalyst concentrations was limited by lower rates of esterification. A virtually constant amount of methanol (approximately 9 moles) is required to volatilize lactic acid from its 82% solution (with 1 ml. of concentrated sulfuric acid per mole of lactic acid as catalyst) except at extremely low rates of methanol feed and presumably at certain high rates of feed.

The catalyst concentration affects the volume of methanol required to volatilize lactic acid (Figure 3). When the catalyst concentration is below 0.25 ml. of sulfuric acid per mole of lactic acid, considerably more methanol is required to carry over the lactic acid. No doubt the explanation is found in the fact that the esterification reactions are slower at the lower catalyst concentrations.

Figures 4 and 5 show that more time and more methanol are required to volatilize a given amount of lactic acid from the more dilute solutions (methanol feed rate was about 8 ml. of liquid per minute, and 1 ml. of concentrated sulfuric acid per mole of lactic acid was used as catalyst). For example, 450 and 600 ml. of methanol, respectively, were required to volatilize 1 mole of lactic acid from its 82 and 50% solutions. Figures 4 and 5 suggest that distillation of water occurs to a considerable extent in the earlier stages and that volatilization of lactic acid takes place more readily after the water concentration is lowered.

A straight line was obtained by plotting the reciprocal of the methanol feed rate (milliliters per minute of liquid methanol) against the time in minutes required to volatilize 90% of the lactic acid (data taken from Figure 1). The relation between the rate of methanol feed and the time in minutes required to volatilize 90% of the lactic acid, starting with 1 mole of 82% lactic acid, is given by the equation which follows.

$$1/(\text{feed rate}) = 0.00271 \text{ time}$$

By using the data of Figure 4, it was found that the time in minutes required to volatilize 90% of the lactic acid is a straight-line function of the reciprocal of the lactic acid concentration (rate of methanol feed, 8 to 8.3 ml. of liquid methanol per minute). The time required to volatilize 90% of the lactic acid from solutions of various concentrations (containing 1 mole of acid) can be calculated from the equation:

$$1/(\text{concentration of lactic acid}) = 0.00061 \text{ time} - 0.0174$$

By this equation it was calculated that 200 minutes would be required to volatilize 90% of the acid contained in 1 mole of 9.6% lactic acid. Approximately 41 minutes would be required to volatilize an equivalent amount of lactic acid from the completely polymerized acid.

ACKNOWLEDGMENT

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